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π-COMPLEX MECHANISM OF CATALYSIS: THE ARYL-COUPLING REACTION

By

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Accorded an A. Cressy Morrison Award in Natural Science in 1960
by The New York Academy of Sciences

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Introduction

A coupling reaction[1] may be defined as one in which two molecules of a Grignard reagent, RMgX (R = aryl), yield one molecule of a compound R-R with the use of a transition metal halide. There are two types of coupling reaction: the stoichiometric reaction, in which the transition metal halide is used in large quantity; and the catalytic reaction, in which the halide (3 to 5 moles per cent) is sufficient to effect coupling.

The mechanisms[2-3] heretofore proposed for such coupling reactions are ambiguous and lack conclusive evidence. The successful elucidation[4] of the structures of Hein's compounds* as π-complexes has led to an insight into the mechanism of the coupling reaction. A new interpretation of the coupling mechanism recently obtained on the basis of experimental evidence is described herein.

Mechanism of the Stoichiometric Coupling Reaction

The original stoichiometric reaction, reported in 1914,[6] is the production in quantitative yield of biphenyl upon the refluxing of an ether solution of phenylmagnesium bromide with chromium chloride. Many other such coupling reactions catalyzed by transition metals are summarized in TABLE 1.

Recent work by my colleagues and myself has indicated that the stoichiometric coupling reaction proceeds in the following manner. In the first stage of the reaction of mesityl magnesium bromide with chromous chloride in tetrahydrofuran, dimesitylchromium tetrahydrofuranate[8] I was proved to form by its isolation as purple crystals (Reaction 1 in FIGURE 1). Although diphenylchromium II was not isolable from the similar reaction of phenylmagnesium bromide and chromous chloride, bisbenzene-chromium (0) IV and benzene-biphenyl-chromium (0) VI were isolated as the products (Reactions 2 and 3 in FIGURE 1), presumably, of the rearrangement of diphenylchromium tetrahydrofuranate.

It was also quite well established by us that, in the second stage of

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*For up-to-date reviews of Hein's original work see Cotton[5a] and Emeleus and Anderson.[5b]

TABLE 1

YIELDS OF BIPHENYL IN COUPLING REACTIONS OF TRANSITION METALS[7]

Metallic halide	Quantity of metallic halide (moles)	C_6H_5MgI (moles)	Yield of biphenyl (%)
$CrCl_3$	0.01	0.03*	98
$CrCl_2$	0.01	0.02*	98
$MnCl_2$	0.01	0.02*	98
$FeCl_2$	0.01	0.02	98
$CoBr_2$	0.01	0.03	98
$NiBr_2$	0.03	0.095	100
$RuCl_3$	0.0036	0.013	99
$RhCl_3$	0.0036	0.013	97
$PdCl_2$	0.0057	0.0163	98
$OsCl_3$	0.0028	0.07	53
$IrCl_3$	0.003	0.01	28
$PtCl_4$	0.006	0.06	6

*C_6H_5MgBr was used.

the reaction of phenylmagnesium bromide and chromous chloride, homolytic cleavage between the carbon and iron atoms takes place to form the hypothetical diradical π-complex III or the half-sandwich π-complex V. Divalent chromium is reduced to zerovalent chromium at this stage, a two-electron reduction.

In the final stage of the reaction, biphenyl is produced by the decomposition of the half-sandwich (V) under rather vigorous reaction conditions, such as refluxing the reaction mixture in benzene. Under milder conditions, such as those Hein used (reaction temperature below $-10°$ C.), the radical complex III and the half-sandwich V should provide sandwich (German *Doppelkegelstructure* or Japanese *tsuzumi*[10]) compounds IV and VI by hydrolysis, or by further reaction with the Grignard reagent followed by hydrolysis.

As a transitional state of diphenylchromium to the π-complexes III or V, between the first and the second steps of the reaction of phenylmagnesium bromide and chromous chloride, the formation of a π-radical electron hybridization complex (a π-radical hybrid shown as in FIGURE 2) is now proposed. The representation pictured in VII for this π-radical hybrid attempts to visualize the transition state of the fission between chromium and the carbon atoms and the formation of π-bonding between the chromium atom and the benzene rings. In this stage the two phenyl groups tilt facing the metal atom, which most probably is not located exactly at the center between the benzene rings. The assumption of the existence of such a π-radical hybrid complex plays an important role in

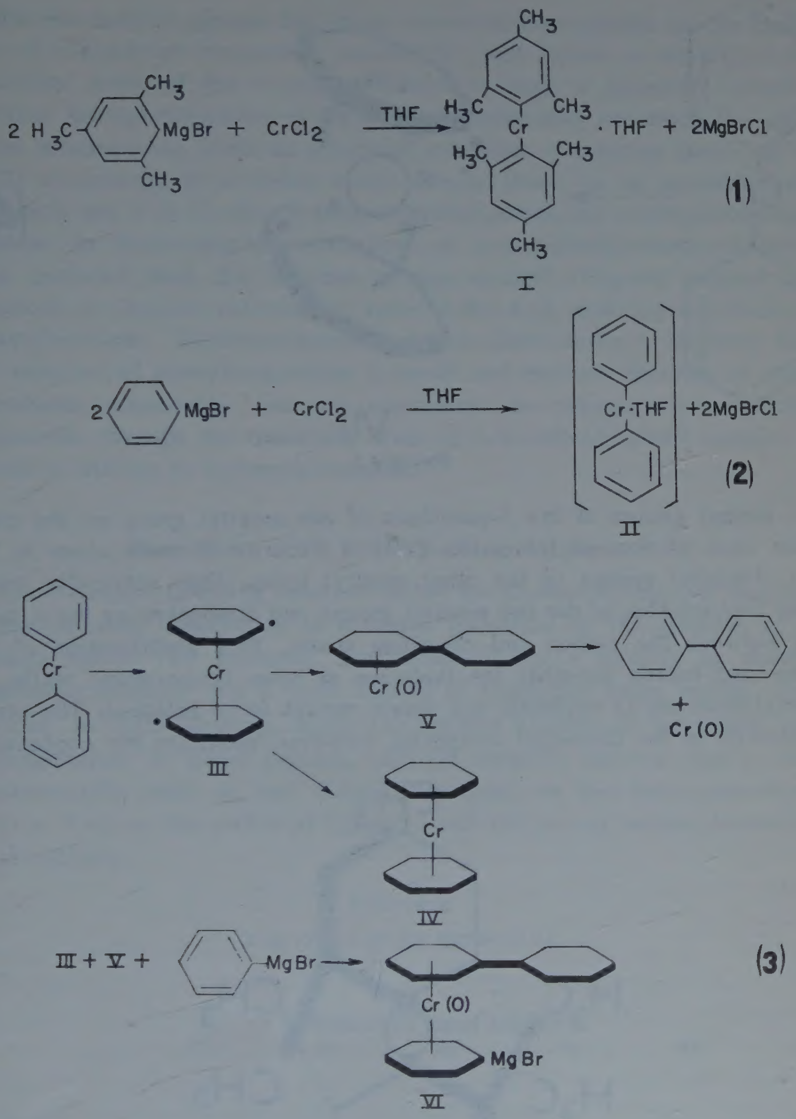
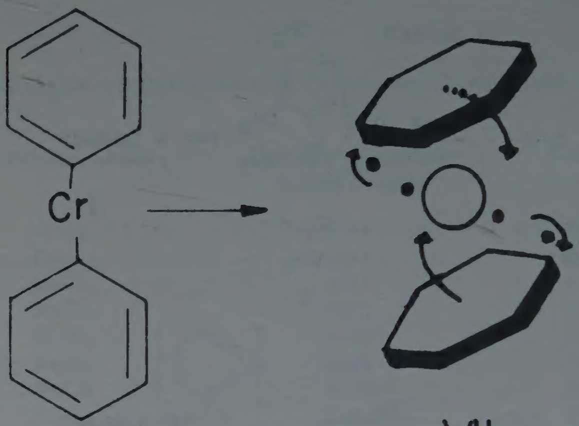


FIGURE 1

the interpretation in a straightforward way of the mechanism of the coupling reaction, particularly of the catalytic type.

This assumption also aids greatly in explaining the coupling reaction involving dimesitylmetal. Neither bis-mesitylchromium nor mesityl-bi-mesityl-chromium π-complexes were obtained from the rearrangement of dimesitylchromium, but bimesityl was yielded almost quantitatively. The

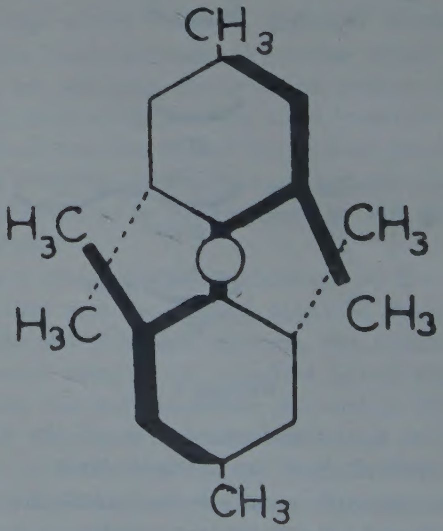


(4)

VII

FIGURE 2

two methyl groups at the β-positions of one mesityl group on the chromium atom of dimesitylchromium (VIII in FIGURE 3) come close to the two β-methyl groups of the other mesityl group, thus sterically inhibiting free rotation of the two mesityl groups and strengthening the α-bonding between the carbon and chromium atoms. This stabilization of the compound makes possible its isolation at room temperature, while diphenylchromium is evidently not stable enough to be isolated. The steric hindrance in the dimesityl compound, however, prohibits the coplanarity



VIII

FIGURE 3

of the two mesityl groups that is an essential requirement for the formation of a sandwich compound, particularly just before or exactly at the transition state of the π-radical hybrid. In such a dimesityl coupling reaction the rearrangement of dimesitylchromium may not reach the stage of an intermediate, such as a radical sandwich π-complex (such as III in 3) supposedly at a stable lower energy level, or an unstable half-sandwich (as V in 3) after π-radical hybridization; no π-complexes comparable to bis-mesitylene-chromium or mesitylenebimesityl-chromium were isolated from the reaction of the mesityl Grignard reagent and chromous or chromic chloride, in spite of the high stability of bis-mesitylene-chromium. Triphenylchromium tetrahydrofuranate,[11] isolated from the reaction of phenylmagnesium bromide and chromic chloride in tetrahydrofuran, reasonably can be considered to rearrange to sandwich compounds through the transition state of a π-radical hybrid complex in a fashion similar to diphenylchromium.

Mechanism of the Catalytic Coupling Reaction

The catalytic coupling reaction called the Kharasch-Grignard reaction[2] is the vigorous stimulation of biphenyl formation by the addition of an organic halide (for example, bromobenzene) to a mixture of phenylmagnesium bromide and a trace amount of transition metal halide. This reaction is quite striking, since (1) organic halides do not react with arylmagnesium or metal halides, and (2) metallic halides couple stoichiometrically with an aryl Grignard reagent, as has been described. TABLE 2 shows the yields of biphenyl with the use of various transition metal halides.

TABLE 2

THE YIELDS OF BIPHENYL

	Transition metal halides					
	Cu	Cr	Mn	Fe	Ni	Co
Yield of biphenyl (%)	6	7	21	47	72	86

The following chain mechanism based on catalysis by "cobaltous subhalide (·CoCl)" was postulated by the Kharasch school of investigators:

$$\phi MgBr + CoCl_2 \rightarrow \phi CoCl + MgBrCl \quad (5)$$

$$2\,\phi CoCl \rightarrow \phi\text{-}\phi + 2\,\cdot CoCl \quad (6)$$

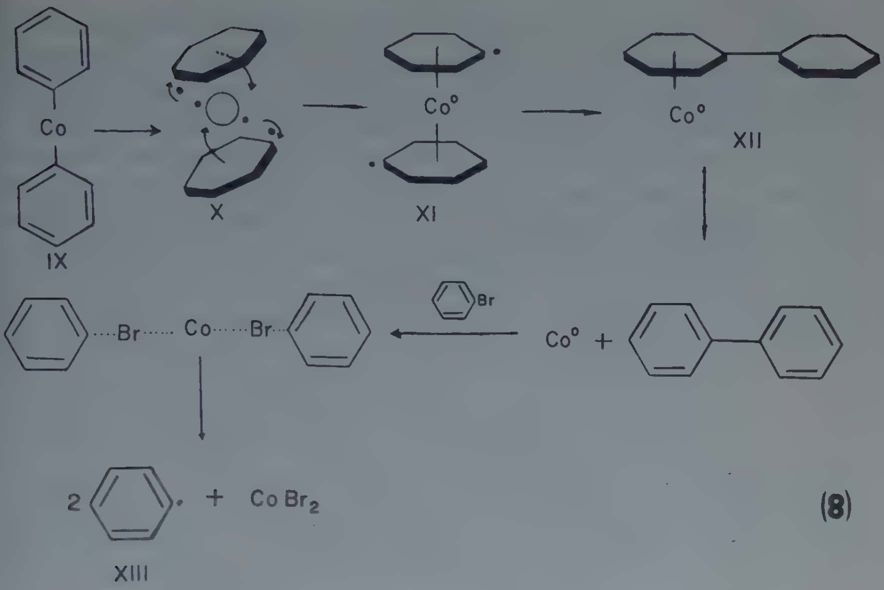
$$\cdot CoCl + \phi Br \rightarrow CoClBr + \phi\cdot \quad (7)$$

Since the substitution of an alkyl halide for an aryl halide also stimulates this coupling reaction, yielding almost the same amount of biphenyl, it is evident that phenyl radicals from bromobenzene (7) actually are not incorporated into the coupling product, biphenyl.

The above subhalide mechanism has been disputed by several groups,[3,13] particularly on the basis of the different behavior of phenyl radicals yielded from phenylcobalt chloride (6) and halobenzene (7). These groups have postulated that unstable diarylcobalt is formed at the first stage of the reaction of the arylmagnesium halide and cobaltous halide; this diarylcobalt then decomposes to form active metallic cobalt that reacts further with the organic halide to yield cobaltous halide.

As has recently been shown experimentally[8] by our group, diphenyl cobalt is definitely formed in the first stage of the reaction of phenylmagnesium bromide and cobaltous chloride, but phenylcobalt chloride is not, particularly in the presence of a large excess of Grignard reagent as in the Kharasch-Grignard reaction. Dimesityl cobalt tetrahydrofuranate,[14] from the reaction of mesitylmagnesium bromide and cobaltous chloride in tetrahydrofuran, was also isolated and characterized by cleavage of the bond between the mesityl groups and the cobalt atom by mercuric chloride, followed by the determination of the amount of mesitylmercuric chloride and cobalt formed. This evidence apparently concludes the argument as to whether cobalt subhalide or diarylcobalt is formed in the first step of the reaction between cobaltous chloride and an aryl Grignard reagent. The most reasonable explanation of the mechanism of this coupling reaction is the now-proposed rearrangement of diphenylcobalt IX to a half-sandwich π-complex XII, through a π-radical hybrid X and diradical π-complex XI, proceeding in a fashion similar to that of the stoichiometric coupling reaction previously described (8 in FIGURE 4).

Nascent metallic cobalt produced from the destruction of the half-sandwich XII may react with bromobenzene to yield cobaltous bromide and *phenyl radicals* XIII not involving any π-radical hybridization, now proposed to be essential for the metal catalysis of the aryl-coupling reaction. This cobaltous bromide reacts further with phenylmagnesium bromide, which exists in much larger amounts than the cobaltous bromide, so that the reaction then proceeds in a catalytic chain fashion as shown in reaction scheme 8. The nascent cobalt metal is here considered to be more reactive than the pyrophoric or colloidal forms of cobalt metal, the reactivity of which with organic halides has been the subject of much disagreement.[15] It has been reported[16] that fine iron powder, washed with dilute hydrochloric acid, water, alcohol, and then with ether, reacts with ethyl bromide in ether at room temperature, the reaction proceeding to completion in 10 to 15 min. The product, claimed to be $(C_2H_5)_2$ FeBr · $C_2H_5FeBr_2$, was obtained in about 10 per cent yield. It was also reported



(8)

FIGURE 4

that bromobenzene reacts in a similar manner with iron powder. This result definitely demonstrates the reactivity of transition metals with organic halides, even when the metals are not in the active pyrophoric, colloidal, or nascent states.

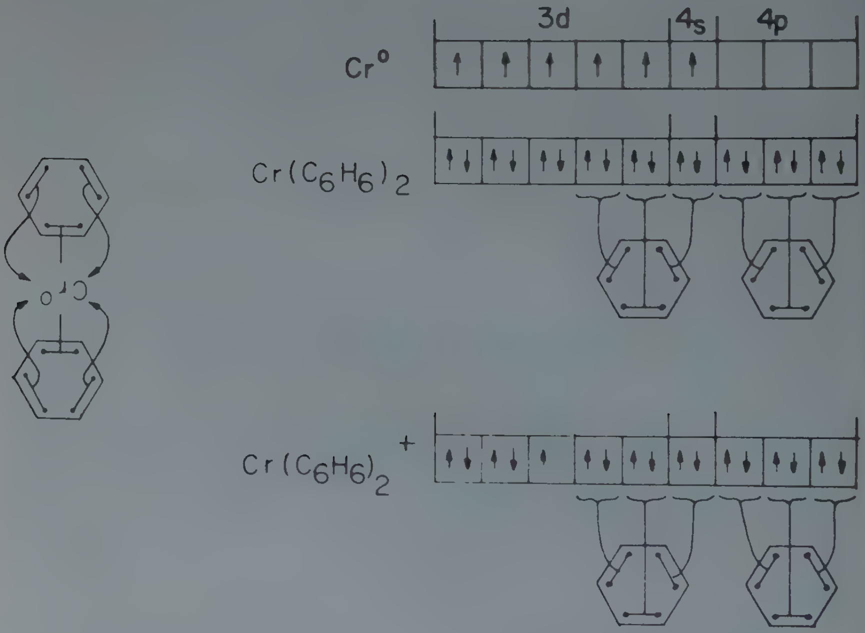
Wang and Yang,[13] members of the Kharasch school, recently reported strong experimental evidence in favor of the reduction of divalent cobalt to the zerovalent state in the Kharasch-Grignard reaction. Although it is apparent that such reduction must occur from the previous discussion, the following additional conclusive evidence bearing on this point has been obtained by us:

1. Bis-benzene chromium (0) and benzenediphenyl chromium (0) were produced without the formation of even a trace of arene chromium (monovalent) π-complex by hydrolysis under a nitrogen atmosphere, with completely oxygen-free water, of the reaction mixture of phenylmagnesium bromide and chromous chloride,[8] as shown in 3.

2. Dimesitylcobalt[14] reacts with 2-butyne to yield hexamethylbenzene, in catalytic fashion, and bis-hexamethylbenzene cobalt, which was isolated as the monovalent π-complex by hydrolysis with water in an air atmosphere. When hydrolysis was carried out with oxygen-free water under a nitrogen atmosphere, the zerovalent π-complex was yielded without formation of any monovalent complex.

The two key factors involved in understanding the efficiency of transition metal catalysis as indicated in TABLE 2 will now be discussed.

Stability of the π-radical hybrid and the radical π-complex. In the stoichiometric coupling reaction, the rearrangement of the aryl transition metal passes through the transitional intermediate π-radical hybrid, at the highest excited energy level, to the radical π-complex, in a more stable lower energy level (3 and 4). Concerning the electron configuration of bis-arene-π-complexes, it is widely accepted by many investigators that the metal attains the inert gas structure. For example, bis-benzene chromium may have an inert gas electron configuration of the octahedral form in which six π-electrons from each benzene ring (a total of 12 π-electrons) fill the empty shell of zerovalent chromium (9 in FIGURE 5).



(9)

FIGURE 5

The stabilization of the radical π-complex of chromium by acceptance of the inert gas (krypton) electron configuration seems to be apparent if one considers the diminution of the catalytic capability of chromium in the catalytic coupling reaction. In the aryl-coupling reactions of manganese, iron, nickel, copper, and cobalt (with the exception of chromium), as shown in TABLE 2, aryl groups may couple immediately after π-radical hybridization without reaching the stable state of the radical π-complex, which should possess an inert gas electron configuration. The stability of a π-radical hybrid of metals is most likely due to satisfaction, as closely as possible, of the requirement for an inert gas electron configuration. This generalization aids in interpreting the efficiency of the transition metal catalysts shown in TABLE 2, with the exception of copper.

Stability of the transition metal-carbon bond. The stability of the transition metal-carbon bond may well explain the exceptional case of copper, in which the efficiency of catalysis is much lower than with the other metals. Aryl and alkyl transition metal derivatives, in general, seem to be very unstable at room temperature. This instability appears to be due to the fact that the d-orbitals in their penultimate shells are on an energy level close to that of their valency s- and p-orbitals.[12] It has been possible to isolate a number of fairly stable complex alkyl and aryl derivatives of group VIII metals by adjusting the energy levels of the d-orbitals by coordination with such ligands as tetrahydrofuran[9,11] and trialkyl or aryl phosphine.[12] The relative stability of the tetrahydrofuranates of aryl (phenyl and mesityl) chromium, manganese, iron, cobalt, nickel, and copper have been investigated (TABLE 3). Aryl iron and nickel tetrahydrofuranates decompose below 0° C. Diphenylcobalt tetrahydrofuranate starts to decompose below –10° C., while dimesitylcobalt tetrahydrofuranate decomposes at 30° C. Chromium tetrahydrofuranate rearranges to a black radical π-complex below room temperature, while dimesitylchromium tetrahydrofuranate is decomposed by refluxing. Diphenylmanganese tetrahydrofuranate gradually decomposes at the boiling point of tetrahydrofuran, while dimesitylmanganese tetrahydrofuranate is stable at that temperature. Aryl (phenyl and mesityl) copper tetrahydrofuranates are stable at the boiling point of tetrahydrofuran. Hydrolysis of the aryl (phenyl and mesityl) transition derivatives with water gives only benzene and mesitylene and not coupling products. This stability of aryl

TABLE 3

(A) Relative stability of diphenyl transition metal tetrahydrofuranates

Metal	Fe	Ni	Co	Cr	Mn	Cu
Decomp. (°C.)	<–10°	<–10°	<–10°	radical π-complex ca. 40°	65°	stable at 65°

(B) Relative stability of dimesityl transition metal tetrahydrofuranates

Metal	Fe	Ni	Co	Cr	Mn	Cu
Decomp. (°C.)	<–10°	<–10°	room temp.	65°	stable at 65°	stable at 65°

copper may be the essential reason why the efficiency of catalysis of copper is lower than that of the other transition metals.

Stability of the transition metal-carbon bond may also be the explanation for the appreciably decreased yields of biphenyl from the stoichiometric coupling reaction of aryl osmium, iridium, and platinum, as shown in TABLE 1. Gilman and Lichenwalter[7] have also considered such an explanation for the inefficiency of coupling of these metals.

Recapitulation

To summarize: the most probable pathway of the course of the mechanism of the stoichiometric and the catalytic coupling reactions has been described in a straightforward way, supported by experimental evidence. It is concluded that a divalent diaryltransition metal forms in the first stage of the reaction of an aryl Grignard reagent and a divalent transition metal halide. In the second stage of such a coupling reaction, the diarylmetal rearranges to a π-radical hybrid, a transition state, which then may be stabilized as a diradical sandwich π-complex, an intermediate of the reaction, if the electron configuration of the hybrid is capable of completing the inert gas electron configuration seen in the case of chromium. Increase of the stability of a π-radical hybrid by the assumption of an electron configuration close to that of an inert gas diminishes the efficiency of the metals as catalysts, particularly in the catalytic coupling reaction. The divalent metal is reduced at this point to the zerovalent state. The influence of steric factors on the coupling reaction is also discussed. Steric hindrance, as in the case of a dimesitylmetal (even of chromium), prohibits the coplanarity of the two mesityl groups that is an essential requirement for the formation of a diradical sandwich. The mesityl groups may then couple immediately after the transition state of π-radical hybridization without passing through the stage of an intermediate diradical sandwich π-complex.

Assessment of the relative strengths of the metal-carbon bonds obtained from experimental observations makes possible an interpretation of the efficiency of catalysis: an increase in the strength of this bond diminishes the capability of the metal to serve as a catalyst in either the stoichiometric or catalytic coupling reactions. Steric factors also provide significant contributions to the explanation of the stability of the bond between carbon and a transition metal. In the case of a dimesityl transition metal, free rotation of the two mesityl groups on the metal is inhibited by the four methyl groups at the β-position, thus strengthening the α-bond between carbon and the metal. A highly stable dimesityl transition metal tetrahydrofuranate (for example, manganese or copper) does not couple even under vigorous conditions, such as refluxing.

The most important proposal of the foregoing discussion is the suggestion that the essential requirement of either a stoichiometric or a catalytic coupling reaction is π-radical hybridization, a transition state in the rearrangement of the diarylmetal. If the aryl group has no chance to form such a π-radical hybrid, coupling will be negligible.

Experimental

Attempts to rearrange dimesitylchromium tetrahydrofuranate to π-complex. Dimesitylchromium tetrahydrofuranate was prepared from the reaction of mesitylmagnesium bromide and chromous chloride in tetrahydrofuran.[8] The following procedures, used for rearrangement of triphenyl chromium tetrahydrofuranate to π-complexes,[11] have been applied in the case of dimesitylchromium:

(1) A tetrahydrofuran solution of dimesitylchromium was refluxed under nitrogen for several hours until the purple color changed to brownish-black. Hydrolysis of the solution gave bimesityl, but not even a trace of any π-complexes.

(2) Removal of tetrahydrofuran from the solid purple dimesitylchromium tetrahydrofuranate under high vacuum resulted in a black solid. Hydrolysis of the black material gave bimesityl, but no trace of any π-complexes.

(3) Heating dimesitylchromium tetrahydrofuranate crystals at 70° C. for one hour under nitrogen, or treatment of the crystals with a large amount of ether, gave a black material that, on hydrolysis, yielded bimesityl but no trace of any π-complexes.

Reaction of dimesitylcobalt and 2-butyne. To a slurried solution of cobaltous chloride (1.30 gm., 0.01 mol.) in 50 ml. of tetrahydrofuran, 21 ml. of mesitylmagnesium bromide (0.95 *M* concentration, 0.02 mol.) was added dropwise while the reaction temperature was kept below –50° C. A light yellowish-green solid precipitated, and the reaction mixture almost solidified. The reaction mixture was shaken vigorously to loosen the solids to a slurried solution. 2-Butyne (6 mol.) was added to the solution at a temperature of –50° C., causing instant decomposition of the yellowish-green material. The temperature was gradually raised to room temperature over a 4-hour period, with efficient stirring, and the mixture was stirred at room temperature overnight. The reaction mixture was refluxed for 30 min. and tetrahydrofuran was then removed under reduced pressure. Benzene (150 ml., oxygen-free) was added to the residue, followed by hydrolysis through the addition of 50 ml. of water (oxygen-free). *The clear water layer contained no π-complexes.*

The dark-brown benzene solution was shaken with water under an air atmosphere. Bis-hexamethylbenzene cobalt $^{+I}$ oxidized by the air was extracted with water. The yield of π-complex was 20 per cent (based on cobalt). Removal of the benzene left hexamethylbenzene, with a yield of 50 per cent (based on cobalt).

Thermal stability of aryl chromium, manganese, iron, cobalt, nickel, and copper tetrahydrofuranate. To a slurried solution of either chromous chloride, manganese chloride, iron chloride, cobalt chloride, nickelous chloride, or cupric chloride (0.01 mol. each) in 50 ml. of tetrahydrofuran, a tetrahydrofuran solution of phenyl or mesityl magnesium bromide (0.02 mol.) was added dropwise while the reaction temperature was kept from –30° to –70° C., depending on the stability of the aryl transition metal tetrahydrofuranate.

Diphenyl and dimesityl iron and nickel tetrahydrofuranates (deep reddish-brown) were not isolable, since they start to decompose below -10° C. Diphenylmanganese tetrahydrofuranate (beige color) decomposes at the boiling point of tetrahydrofuran while the dimesityl derivative (beige color) is stable at this temperature. Diphenylcobalt tetrahydrofuranate decomposes below -10° C., while the dimesityl derivative is stable up to 30° C.

Acknowledgment

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